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The Alternative Model of Water Vapour Sorption in Porous Building Materials

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Abstract Mathematical modelling of water sorption in porous building materials is considered. The explanations of inadequacies of both Brunauer–Deming–Deming–Teller model for the high relative humidities range and Frenkel–Halsey–Hill model for the low relative humidities range reported by Pavlík et al. (Transp. Porous Med. 91:939–954, 2012) are proposed. The generalized D'Arcy and Watt (GDW) model is proposed as a simpler alternative for a procedure of experimental isotherms fitting proposed by Pavlík et al. The suitability of the GDW equation to describe the water sorption isotherms in the building materials for the whole range of relative humidities is confirmed.

Keywords Porous building materials · Water sorption · Mathematical modelling · GDW model

Recently, Pavlík et al. (2012) studied water sorption in porous building materials. They analysed experimental isotherms using a few theoretical models [i.e. BET, Brunauer–Skalny–Bodor (BSB), Brunauer–Deming–Deming–Teller (BDDT) and Frenkel–Halsey–Hill (FHH)]. They stated the BSB equation was found to provide a good approximation for the relative humidities (h_r) below 0.6–0.7, whereas the FHH equation showed a sufficient accuracy for the h_r above 0.4–0.5. Pavlík et al. (2012) proposed also to use the combination of BSB and FHH isotherms to obtain a very accurate approximation of experimental data for the whole h_r range.

The inadequacy of FHH model for low values of h_r is due to its mathematical form. This equation of Halsey type in the limit $h_r \rightarrow 0$ does not reduce to the linear Henry's isotherm (Furmaniak et al. 2009). On the other hand, the II type isotherms (as observed by Pavlík et al. 2012) may be regarded as the sum of isotherms of I type (i.e. Langmuirian) and III type (Blahovec and Yanniotis 2009; Furmaniak et al. 2011). These types of isotherms are connected with adsorption on primary (i.e. present on the sorbent surface) and

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secondary (i.e. created after molecules are sorbed on primary centres) sorption centres, respectively (Furmaniak et al. 2011). The shape of the total isotherm depends on the share of both isotherm types. The BDDT isotherm equation (mathematical equivalent to Guggenheim–Anderson–de Boer (GAB) equation—see for example Furmaniak et al. 2009) assumes the presence of both primary and secondary centres, but in the ratio 1:1 (one H_2O attached to primary centre creates one secondary centre) (Furmaniak et al. 2009, 2011). This fact may explain the inadequacy of the BSB model in the high h_r range reported by Pavlík et al. (2012).

The generalized D'Arcy and Watt model (GDW) is an approach that allows assuming any ratio of sorption of primary and secondary centres (Furmaniak et al. 2009). The GDW isotherm assumes the existence of the primary sorption centres on the adsorbent surface. H_2O molecules bonded to those centres convert into the secondary ones. Such a molecule may create one secondary site but more often a greater or smaller number of centres is created. The form of this equation is (Furmaniak et al. 2009):

$$M = \frac{m_0 K h_r}{1 + K h_r} \cdot \frac{1 - k\,(1 - w)\,h_r}{1 - k h_r} \tag{1}$$

where M is the amount of adsorbed water (the change in sample mass), m_0 is the concentration of primary sites, K and k are the kinetic constants connected with sorption on primary and secondary centres, and w is the parameter determining the ratio of molecules bonded to primary centres and converted into the secondary ones.

The GDW model was used to describe the water sorption isotherms (at 298 K) measured by Pavlík et al. (2012) for different porous building materials (i.e. autoclaved aerated concrete AAC P2-400, lightweight ceramic brick FAMILY 50, phase change material Micronal DS5008 X, lime plaster with Micronal in dosage of 5 %, and old-fashioned type of ceramic brick, labelled as AAC, LCB, PCM, LP and OFCB, respectively). Experimental data were fitted using the genetic algorithm proposed by Storn and Price (1997)—for details see for example (Furmaniak et al. 2009). The goodness of the fit was estimated using the determination coefficient defined as (Furmaniak et al. 2009):

$$\mathrm{DC} = 1 - \frac{\sum_i \left(M_{t,i} - M_{o,i}\right)^2}{\sum_i \left(M_{o,i} - \overline{M}_o\right)^2} \tag{2}$$

where $M_{t,i}$ and $M_{o,i}$ are theoretical and observed moisture content for ith experimental point, and $\overline{M}_o$ is the average observed moisture content. The values of the obtained best-fit parameters are collected in Table 1. Figure 1 shows the graphical representation of results. The fit quality is excellent for the whole range of h_r as proved by, inter alia, high values of DC. Thus, the use of the GDW model may be a simpler alternative to the procedure proposed by Pavlík et al. (2012), which requires a description of the data using two different models and then fitting of the parameters of switching function. In addition, the obtained parameters of the GDW model (similarly as in the case of other models with a strong theoretical basis) allow for the estimation of some parameters characterizing the studied material (as the monolayer capacity (m_0) and the average energy of H_2O surface interactions, which affects the value of the constant K) and give insight into the mechanism of the sorption process (parameter w). For all the considered building materials, the value of parameter w is lower than 1, so the number of created secondary centers is smaller than the number of primary centers (due to, for example, steric effects).

Table 1 The values of the best-fit parameters obtained from the fitting of the experimental data by the GDW model (Eq. 1)

Material	m_0 (%)	K	k	w	DC
AAC	1.47	10.0	0.947	0.190	0.9999
LCB	0.166	1.78	0.982	0.184	0.9995
PCM	0.603	2.80	0.955	0.658	0.9999
LP	1.59	0.984	0.962	0.0934	0.9994
OFCB	0.0619	2.23	0.984	0.0950	0.9985

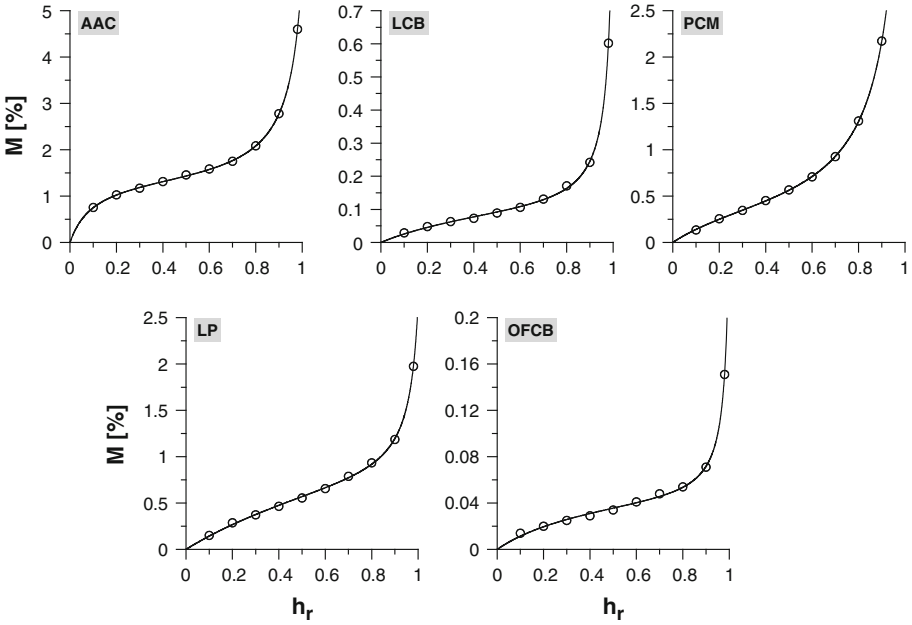

Fig. 1 The results of fitting of the experimental data (published by Pavlík et al. 2012) by the GDW model (Eq. 1), *points* experimental data, *lines* fitting

References

Blahovec, J., Yanniotis, S.: Modified classification of sorption isotherms. J. Food Eng. **91**, 72–77 (2009)

Furmaniak, S., Terzyk, A.P., Gołembiewski, R., Gauden, P.A., Czepirski, L.: Searching the most optimal model of water sorption on foodstuffs in the whole range of relative humidity. Food Res. Int. **42**, 1203–1214 (2009)

Furmaniak, S., Terzyk, A.P., Gauden, P.A.: Some remarks on the classification of water vapor sorption isotherms and Blahovec and Yanniotis isotherm equation. Dry. Technol. **29**, 984–991 (2011)

Pavlík Z. Žumár J. Medved I. Černý R.: Water vapor adsorption in porous building materials: experimental measurement and theoretical analysis. Transp. Porous Med. **91**, 939–954 (2012)

Storn, R., Price, K.: Differential evolution—a simple and efficient heuristic for global optimization over continuous spaces. J. Glob. Optim. **11**, 341–359 (1997)